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Development of a new traceless aniline linker for solid-phase synthesis of azomethines. Application to parallel synthesis of a rod-shaped liquid crystalline library

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Abstract—A new traceless linker was developed to synthesize a library of 42 compounds possessing an azomethine linkage using combinatorial solid-phase parallel synthesis. The loading of the substrates on a solid support and cleavage from the solid support were performed by an imine synthesis and by imine-exchanged process under mild conditions, respectively. Thioesters with a hydroxy group on the central core exhibited liquid crystalline properties with the widest transition temperatures in the library.
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1. Introduction

Solid-phase organic synthesis has been commonly used for combinatorial synthesis to rapidly discover new drugs and materials. Many types of linkers were recently developed in combinatorial solid-phase syntheses because the selection of an adequate linker is important to efficiently build the desired libraries.[1] Linkers should be easy to load starting materials onto the solid support, must be stable during the reactions and must be cleavable without damage to the product at the final stage. Especially, traceless linkers have advantages because the point of attachment on the solid support is not apparent in the target molecules.[2]

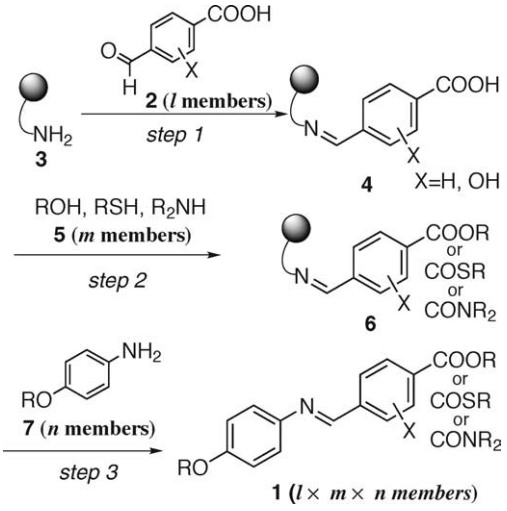
Liquid crystals are widely used in optoelectric devices and electron-transporting materials. Considerable synthetic effort and time are required to develop new liquid crystals. We previously demonstrated an efficient combinatorial synthesis to search for new liquid crystals and to systematically investigate the substitution effect on mesomorphism by preparing liquid crystalline libraries on a solid support.[3–6]

In this paper, we focus on the development of a new traceless linker to synthesize rod-shaped azomethine derivatives,[7] which are typical liquid crystals.[8]

2. Results and discussion

2.1. Development of a new aniline linker and synthesis of a liquid crystalline library

The structure of the target molecules **1** synthesized on the



Scheme 1. Synthetic plan of an azomethine-type liquid crystalline library.

Keywords: Liquid crystals; Combinatorial synthesis; Traceless linker; Azomethines.
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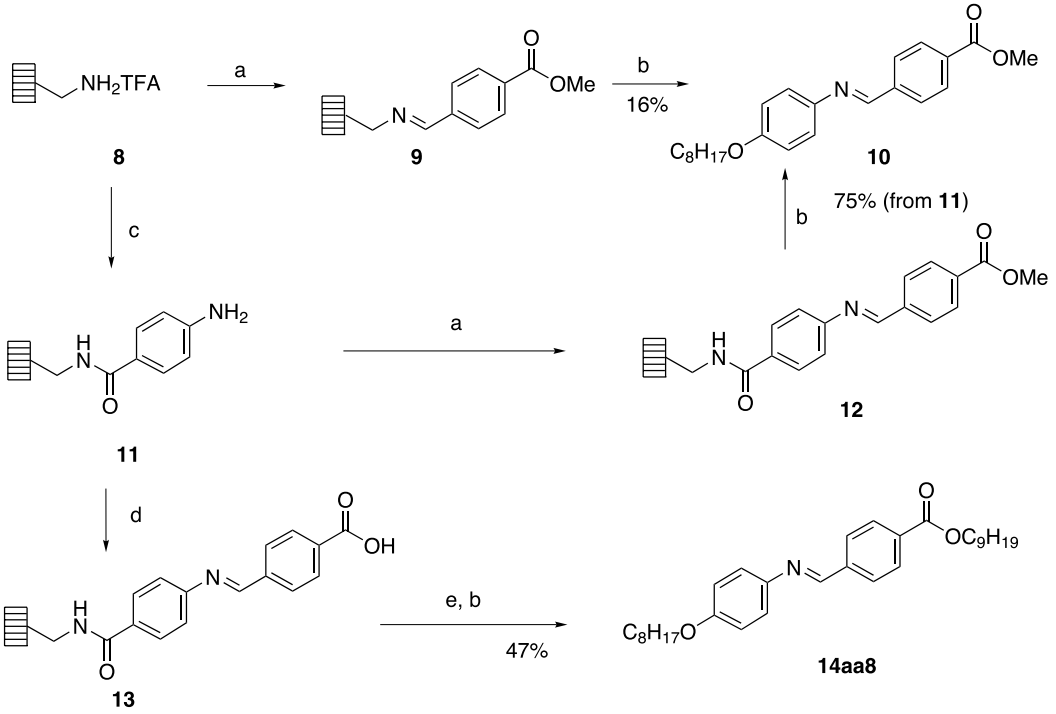
solid phase is shown in Scheme 1. They are composed of a rigid aromatic core with an azomethine linkage, an alkoxy side chain, and an ester or amide group. We planned to construct a liquid crystalline library through solid-phase synthesis by employing imine-exchange reactions[9] because the target molecules **1** have no extra functional groups to attach to the solid support. In addition, because the azomethine linkage is labile to acids and bases, we designed a new linker suitable for synthesizing the liquid crystals with an azomethine linkage on a solid support under mild conditions. In the first step, *l* members of 4-formylbenzoic acids **2** are condensed with an amine **3** on the solid support to afford resin-bound azomethine **4** (step 1). In the second step, *m* members of alcohols, thiols, and amines **5** are reacted with **4** to give azomethine **6** (step 2). Finally, the azomethines on the solid support are cleaved by *n* members of 4-alkoxyanilines **7** through an imine-exchange process to give **1** (step 3). In the consecutive procedure, $l \times m \times n$ members of compounds are synthesized in these three steps.

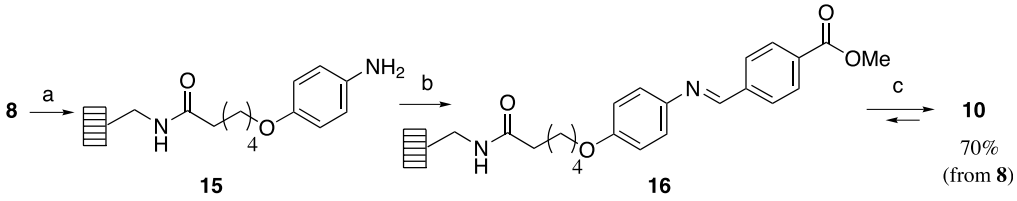
Methyl 4-formylbenzoate was linked to aminomethylated SynPhase Lantern **8**, a multipin solid support, through imine formation to give resin-bound methyl benzoate **9**. 4-Octyloxyaniline was added to proceed to the imine-exchange reaction, which gave the desired product **10** in only 16% yield due to the instability of resin-bound azomethine **9**. To stabilize the resin-bound azomethine, we synthesized a linker **11** from **8** and a 4-aminobenzoic acid derivative. The loading of methyl 4-formylbenzoate and cleavage with 4-octyloxyaniline on the resin **12** gave the azomethine **10** in 75% yield. A three-step procedure involving 4-formylbenzoic acid loading followed by condensation with 1-nonanol and cleavage with 4-octyloxyaniline afforded **14aa8** in 47% yield. This reduced yield might result from partial alcoholysis of a resin-bound azomethine **13** during the condensation step. (Scheme 2)

4-Alkoxyaniline linker **15** was synthesized to stabilize a resin-bound azomethine intermediate. Simple loading and cleavage using **15** gave the desired product **10** in 70% yield. The equilibrium between **10** and **16** was not shifted effectively in favor of **10** due to their comparable stability even addition of 4 equiv of 4-octyloxyaniline. (Scheme 3)

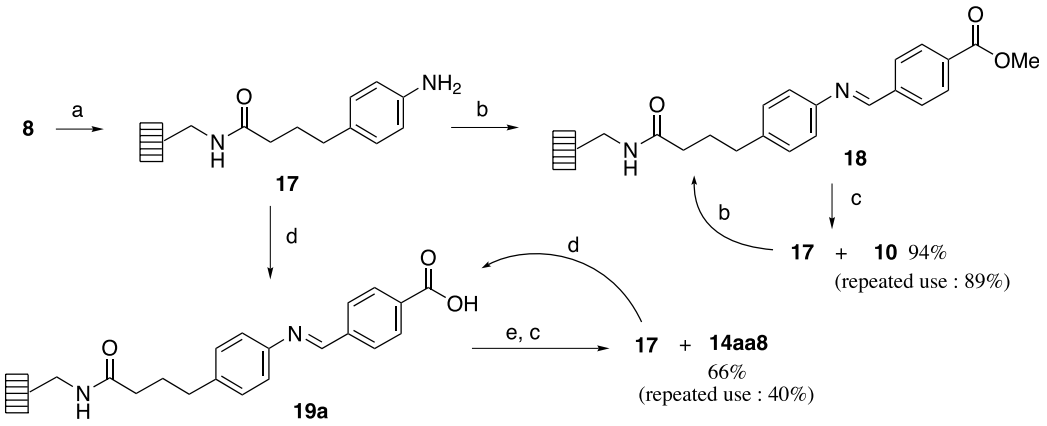
The product yields were dependent on the delicate stability balance of the resin-bound azomethine. The ideal linker should resist alcoholysis during condensation and cause an equilibrium shift favorable to the product in the final step.



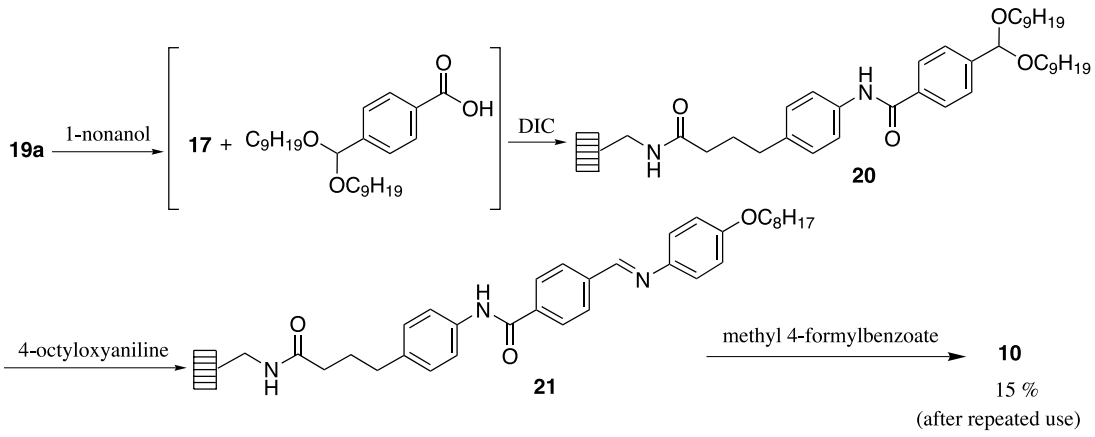
Scheme 2. Model synthesis of azomethines on a solid support from **8** or **11**. Reaction conditions: (a) methyl 4-formylbenzoate, DMF, rt, 24 h; (b) 4-octyloxyaniline, 50 °C, 3 h; (c) 4-*tert*-butoxycarbonylaminobenzoic acid, DIC, HOBt, DCM, then TFA, DCM; (d) 4-formylbenzoic acid, DMF, rt, 24 h; (e) 1-nonanol, DIC, DMAP, DCM, rt, 3 h.



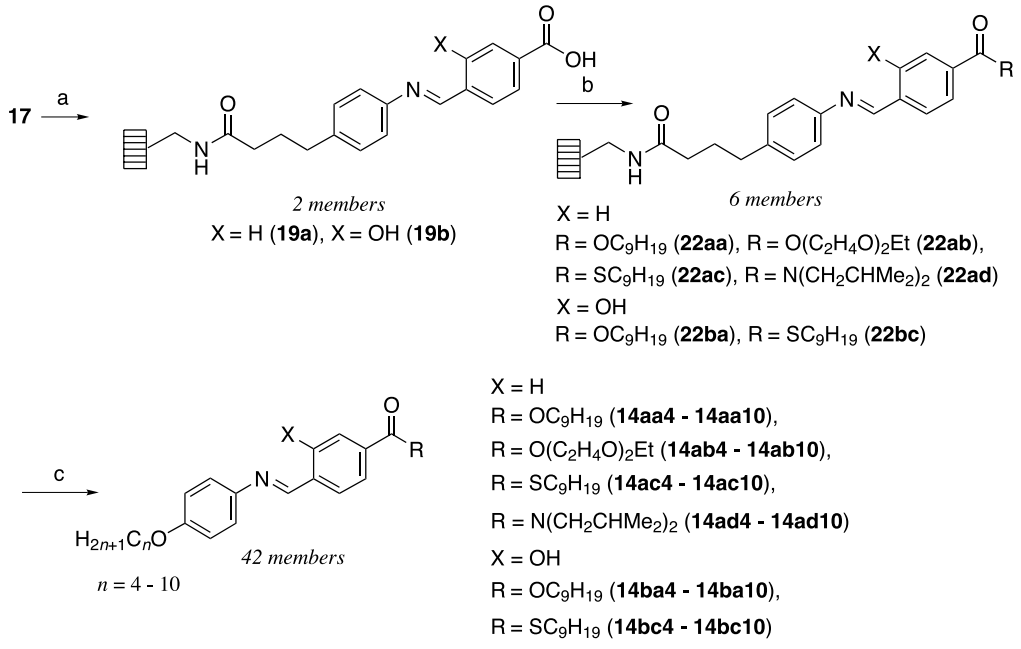
Scheme 3. Model synthesis of azomethine **10** on a solid support using an aniline linker **15**. Reaction conditions: (a) 6-(4-*tert*-butoxycarbonylaminophenoxyl)-hexanoic acid, DIC, HOBt, DCM, then TFA, DCM; (b) methyl 4-formylbenzoate, DMF, rt, 24 h; (c) 4-octyloxyaniline, 50 °C, 3 h.



Scheme 4. Model synthesis of azomethines on a solid support using an aniline linker **17**. Reaction conditions: (a) 4-(4-*tert*-butoxycarbonylaminophenyl)-butyric acid, DIC, HOBt, DCM, then TFA, DCM; (b) methyl 4-formylbenzoate, DMF, rt, 24 h; (c) 4-octyloxyaniline, 50 °C, 3 h; (d) 4-formylbenzoic acid, DMF, rt, 24 h; (e) 1-nonanol, DIC, DMAP, DCM, rt, 3 h.



Scheme 5. Partial alcoholysis and subsequent condensation in the second step.



Scheme 6. Parallel synthesis of an azomethine library on a solid support. Reaction conditions: (a) 2 kinds of 4-formylbenzoic acid (4-formylbenzoic acid, 4-formyl-3-hydroxybenzoic acid), DMF, rt, 24 h; (b) 4 kinds of alcohols, thiol, and amine (n-$C_9H_{19}OH$, $Et(OC_2H_4)_2OH$, n-$C_9H_{19}SH$, $(Me_2CHCH_2)_2NH$), DIC, DMAP, DCM, rt, 3 h; (c) 7 kinds of 4-alkoxyanilines (n=4–10), DMF, 50 °C, 24 h.

Finally, 4-alkylaniline linker **17** was investigated. (Scheme 4) The resin-bound intermediate **18** was expected to have moderate stability between **12** and **16**. The product **10** was obtained in 94% yield by simple loading and cleavage. The three-step procedure involving condensation with 1-nonanol gave **14aa8** in 66% yield.

Because the original linker **17** must be recovered after cleavage of the resin-bound azomethines, we investigated the possibility of recycling of the linker **17**. In the case of simple loading and cleavage, the yield of the repeated using was comparable to the first one. However, the yield decreased considerably from 66 to 40% for the recycling in the three-step procedure. (Scheme 4) To elucidate the details of the reaction occurred on the resin, the recycled resin was treated with methyl 4-formylbenzoate. The methylester **10** was obtained in 15% yield. This result indicates that azomethine **21** was partially formed on the solid support via alcoholysis of **19a** and consecutive condensation in the second step. (Scheme 5).

2.2. Library synthesis of rod-shaped liquid crystals

The linker **17** was most suitable for the synthesis of azomethines on the solid support in our experiment. We applied the linker **17** to parallel synthesis of a rod-shaped liquid crystalline library shown in Scheme 6. 4-Formylbenzoic acid and 4-formyl-3-hydroxybenzoic acid were linked to **17** to afford two members of resin-supported azomethines **19a** and **19b**. The reaction of **19a** with two alcohols, a thiol, and an amine gave the corresponding esters **22aa**, **22ab**, a thioester **22ac** and an amide **22ad**. On the other hand, **19b** was reacted with an alcohol and a thiol to form an ester **22ba** and a thioester **22bc**. Finally, all six members of azomethines are reacted with 7 kinds of 4-alkoxyanilines to afford the 42 final products through imine-exchange reactions. Esters **14aa4–14aa10** (n=4–10) and **14ab4–14ab10** (n=4–10) and thioesters **14ac4–14ac10** (n=4–10) were obtained in moderate yield after chromatographic purification (Table 1). On the other hand, amides **14ad4–14ad10** (n=4–10) were obtained in low yield,

Table 1. Isolated yields and transition temperatures of all library members

Compounds	X	R	n	Yield (%)	Transition temperatures (°C) and enthalpy changes (kJ mol^{-1})[a]
14aa4	H	OC_9H_{19}	4	55	Cr 58.7 (25.2) SmA 81.3 (3.3) Iso
14aa5			5	58	Cr 58.1 (27.0) SmA 76.0 (3.0) Iso
14aa6			6	59	Cr 57.8 (27.6) SmA 84.3 (3.8) Iso
14aa7			7	57	Cr 65.1 (30.4) SmA 84.4 (3.8) Iso
14aa8			8	66	Cr 63.7 (28.1) SmA 88.3 (3.9) Iso
14aa9			9	58	Cr_1 67.8 (12.4) Cr_2 70.4 (15.8) SmC 85.7 SmA 87.6 (4.2) Iso
14aa10			10	55	Cr 75.1 (17.3) SmC 80.7 SmA 89.6 (4.4) Iso
14ab4	H	$O(C_2H_4O)_2Et$	4	71	Cr 74.2 (32.2) [SmA 42.8 (3.1)] Iso[b]
14ab5			5	53	Cr 57.0 (27.5) [SmA 27.5 (2.4)] Iso
14ab6			6	57	Cr 62.2 (31.1) [SmA 40.3 (3.2)] Iso
14ab7			7	58	Cr 43.5 (23.0) [SmA 38.8 (3.0)] Iso
14ab8			8	52	Cr_1 40.0 (5.3) Cr_2 43.5 (15.3) SmA 46.7 (3.9) Iso
14ab9			9	51	Cr 58.4 (28.6) Iso
14ab10			10	60	Cr 56.9 (28.0) Iso
14ac4	H	SC_9H_{19}	4	53	Cr 78.3 (16.7) SmF 82.9 (0.8) SmA 150.8 (3.5) Iso
14ac5			5	58	Cr 72.8 (21.8) SmF 83.4 (1.1) SmC 100.5 SmA 148.5 (3.5) Iso
14ac6			6	82	Cr 70.2 (14.7) SmF 92.7 (1.6) SmC 111.2 SmA 149.8 (4.3) Iso
14ac7			7	52	Cr 75.1 (23.2) SmF 95.2 (1.8) SmC 131.0 SmA 147.8 (4.4) Iso
14ac8			8	53	Cr 76.9 (19.1) SmF 102.4 (2.3) SmC 133.7 SmA 148.7 (4.3) Iso
14ac9			9	33	Cr 87.1 (24.4) SmF 102.6 (2.9) SmC 137.4 SmA 143.5 (4.3) Iso
14ac10			10	33	Cr 90.0 (22.7) SmF 106.6 (3.4) SmC 142.6 SmA 146.1 (5.8) Iso
14ad4	H	$N(CH_2CHMe_2)_2$	4	25	Cr 98.7 Iso
14ad5			5	12	Cr 72.7 Iso
14ad6			6	18	Cr 83.3 Iso
14ad7			7	16	Cr 85.2 Iso
14ad8			8	20	Cr 105.5 Iso
14ad9			9	22	Cr 93.4 Iso
14ad10			10	24	Cr 78.5 Iso
14ba4	OH	OC_9H_{19}	4	47	Cr 70.6 (19.8) SmA 128.7 (4.2) Iso
14ba5			5	46	Cr 73.2 (21.3) SmA 123.8 (4.2) Iso
14ba6			6	52	Cr 77.0 (18.3) SmA 126.7 (4.7) Iso
14ba7			7	50	Cr 76.0 (23.3) SmC 81.0 SmA 124.0 (4.8) Iso
14ba8			8	47	Cr 85.7 (25.4) SmC 99.0 SmA 125.0 (5.0) Iso
14ba9			9	43	Cr 92.0 (27.1) SmC 113.0 (0.2) SmA 123.7 (4.6) Iso
14ba10			10	30	Cr 85.1 (31.6) SmC 118.2 (0.1) SmA 124.3 (5.4) Iso
14bc4	OH	SC_9H_{19}	4	17 (38)[c]	Cr_1 47.8 (1.3) Cr_2 62.7 (8.2) SmA 188.1 (4.4) Iso
14bc5			5	20 (38)	Cr 68.6 (13.6) SmA 185.2 (5.3) Iso
14bc6			6	18 (40)	Cr_1 55.9 (3.3) Cr_2 58.7 (8.8) SmA 185.7 (5.2) Iso
14bc7			7	21 (39)	Cr 60.1 (11.2) SmC 149.0 SmA 182.5 (5.5) Iso
14bc8			8	19 (40)	Cr 64.7 (12.5) SmC 161.0 SmA 182.1 (5.6) Iso
14bc9			9	20 (32)	Cr 71.2 (14.3) SmC 171.0 (0.2) SmA 178.6 (6.1) Iso
14bc10			10	17 (34)	Cr 70.7 (16.1) SmC 173.5 (0.2) SmA 177.6 (6.4) Iso

[a] The transition temperatures and the enthalpy changes shown in parentheses were determined by the second heating of DSC except for **14ad** series. The transition temperatures of **14ad** series were determined by the second heating of optical microscopy.
[b] Mesomorphic phases, transition temperatures and enthalpy changes in brackets were observed in the first cooling process.
[c] Values in parentheses refer to yields for 16 equiv of 1-nonanethiol in step 2.

possibly because the imine-exchange reaction between **19a** and diisobutylamine partially occurs at the second step. The yields of **14b** series (X=OH) were lower than corresponding **14a** series (X=H) probably due to partial self-condensation between a phenolic hydroxy and carboxylic group in **19b** on the resin. Addition of large excess (16 equiv) of thiol at the second step improved the yield in **14bc** series.

2.3. Mesomorphic behavior

The transition temperature and the thermal behavior of the library members were determined using a polarizing microscope equipped with a hot stage and differential scanning calorimetry (DSC) measurement. The results are summarized in Table 1. Esters **14aa4–14aa10** (n=4–10) exhibited smectic A (SmA) and C (SmC) phases, in which the SmA phase was demonstrated by observation of fan and homeotropic textures while the SmC phase was assigned by observation of fan and schlieren textures. The X-ray diffraction study of **14aa10** (n=10) indicated that the layer spacings of the SmA and SmC phases were 34.3 Å at 87 °C and 33.8 Å at 78 °C, respectively. Because the calculated molecular length of **14aa10** (n=10) is 37.1 Å, molecules should partially intercalate in the SmA phase and the molecules are tilted 24 ° in the SmC phase when they form a monolayer arrangement. On the other hand, **14ac10** (n=10) had SmA, SmC, and smectic F (SmF) phases. The SmF phase was assigned by the observation of the mosaic texture. The X-ray diffraction study of **14ac10** (n=10) indicated that the layer spacings of the SmA, SmC, and SmF phases were 33.1 Å at 145 °C, 32.2 Å at 130 °C, and 34.5 Å at 98 °C, respectively. The calculated molecular length of **14ac10** (n=10) is 37.5 Å. The molecular packing models are similar to those of **14aa10** (n=10). The layer spacing of the tilted SmF phase is slightly larger than that of the SmA phase. It might be due to that the SmA phase has more molten side chains than the SmF phase appeared at the lower temperature. Monoethyl diethylene glycol esters **14ab4–14ab10** had a less stable SmA phase monotropically. The reduction of the thermal stability of **14ab4–14ab10** might be due to the flexibility of the diethylene glycol chain. The secondary amides **14ad4–14ad10** were not mesomorphic because of the increase in molecular width of their branching.

Thioesters **14ac4–14ac10** exhibited liquid crystalline properties with the higher thermal stability compared to corresponding esters **14aa4–14aa10**, and **14ab4–14ab10**. The thermal stability of the SmA phase of **14ac4–14ac10** was enhanced by approximately 60 °C when compared with **14aa4–14aa10** because the thioester linkage is superior in linearity and longitudinal length to corresponding ester linkage.[10] The clearing temperature for **14b** series (X=OH) was 40–60 °C higher than that for **14a** series (X=H) as a result of hydrogen bond formation between azomethine nitrogen and phenolic hydrogen, which enhanced the planarity of the molecule.[11] The thioesters possessing a hydroxy group on the aromatic nuclei (**14bc** series, R=SC_9H_{19}, X=OH) showed smectic phase in the widest temperature range.

3. Conclusion

We developed a new traceless linker, which made it possible to synthesize a library of liquid crystals with an azomethine linkage using imine-exchange reactions through combinatorial solid-phase parallel syntheses. This linker has the advantage of being able to release the final product under mild conditions. Thioesters at the terminal position with hydroxy group on the central core exhibited smectic phases with the widest transition temperatures in the library consisting of 42 members. Thermal stability of the library members was explained by consideration of the linearity and planarity of the molecules and flexibility and bulkiness of the substituents of the ester and the amide groups.

4. Experimental

4.1. General

All commercially available chemicals were used without further purification except 4-alkoxyanilines. The 4-alkoxyanilines were further purified by recrystallization. The SynPhase Lantern **8** was purchased from Mimotopes Pty Ltd (Victoria, Australia). Melting points were determined using a Büchi B-545 apparatus and are uncorrected. IR spectra were recorded with a JASCO FT/IR410 spectrophotometer equipped with SensIR Technologies Durascope™ for ATR (attenuated total reflectance) and only characteristic peaks are reported. ^{1}H NMR spectra were recorded at 200 or 300 MHz with Varian Gemini-200 or Mercury-300 spectrometers, using tetramethylsilane as the internal standard. Mass spectra were taken on JEOL AX-500. Elemental analyses were performed using PerkinElmer 2400. The transition temperatures and the mesomorphic phase were observed by a polarizing microscope (Olympus BHSP BH-2) equipped with a hot stage (Linkam TH-600RMS). Enthalpy changes were measured using a differential scanning calorimeter (Seiko DSC 200). The X-ray diffraction measurements were carried out with a Rigaku Rint 2100 system using Ni-filtered Cu Kα radiation at various temperatures. The measuring temperatures were controlled with a Linkam HFS-91 hot stage.

4.2. Preparation of aniline linkers 11, 15, and 17

4.2.1. Ethyl 6-(4-*tert*-butoxycarbonylaminophenoxy)hexanoate. To a mixture of ethyl 6-[(4-methylbenzenesulfonyl)-oxy]hexanoate[12] (1.09 g, 3.47 mmol) and potassium carbonate (1.67 g, 12.1 mmol) in acetonitrile (5 mL) was added *N*-Boc-4-hydroxyaniline (0.722 g, 3.45 mmol) in acetonitrile (5 mL). The reaction mixture was heated at reflux for 17 h. After being cooled to room temperature, the reaction was quenched by addition of saturated aqueous NH_4Cl (10 mL). The mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were dried over sodium sulfate and concentrated to furnish the crude product, which was purified by flash chromatography (silica gel 45 g, ethyl acetate/hexane 1:5) followed by recrystallization (ethyl acetate/hexane) to give the product (776 mg, 2.21 mmol, 64%) as a colorless needles: mp 73.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (3H, t, J=

7.1 Hz), 1.44–1.57 (2H, m), 1.51 (9H, s), 1.69 (2H, quint, J=7.4 Hz), 1.78 (2H, quint, J=6.3 Hz), 2.33 (2H, t, J=7.4 Hz), 3.92 (2H, t, J=6.3 Hz), 4.13 (2H, q, J=7.1 Hz), 6.34 (1H, br s), 6.82 (2H, d, J=8.8 Hz), 7.24 (2H, d, J=8.8 Hz); IR (ATR) 3364, 1733, 1690 cm^{-1}; MS (CI): *m/z* 296 (100%), 351 ($[M]^+$, 59%); HRMS (CI): calcd for $C_{19}H_{29}NO_5$ ($[M]^+$), 351.2046, found 351.2057. Anal. Calcd for $C_{19}H_{29}NO_5$: C, 64.93; H, 8.32; N, 3.37. Found: C, 65.21; H, 8.55; N, 4.14.

4.2.2. 6-(4-*tert*-Butoxycarbonylaminophenoxy)hexanoic acid. To a solution of ethyl 6-(4-*tert*-butoxycarbonylaminophenoxy)hexanoate (776 mg, 2.21 mmol) in ethanol (12 mL) was added 1 M NaOH solution (4 mL). The reaction mixture was stirred at room temperature for 10 h and quenched by addition of saturated aqueous NaH_2PO_4 (10 mL). The mixture was extracted with ethyl acetate (3× 15 mL). The combined organic layers were dried over sodium sulfate and concentrated to give the crude product, which was purified by flash chromatography (silica gel 30 g, ethyl acetate) and followed by recrystallization (ethyl acetate/hexane). The product (575 mg, 1.78 mmol, 81%) was isolated as a colorless needles: mp 115 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45–1.57 (2H, m), 1.51 (9H, s), 1.71 (2H, quint, J=7.6 Hz), 1.79 (2H, quint, J=6.3 Hz), 2.39 (2H, t, J=7.6 Hz), 3.92 (2H, t, J=6.3 Hz), 6.45 (1H, br s), 6.81 (2H, d, J=8.9 Hz), 7.23 (2H, d, J=8.9 Hz); IR (ATR) 3362, 1697, 1672 cm^{-1}; MS (CI): *m/z* 268 (100%), 323 ($[M]^+$, 62%); HRMS (CI): calcd for $C_{17}H_{25}NO_5$ ($[M]^+$), 323.1733, found 323.1727. Anal. Calcd for $C_{17}H_{25}NO_5$: C, 63.14; H, 7.79; N, 4.33. Found: C, 63.35; H, 8.01; N, 4.51.

4.2.3. 6-(4-*tert*-Butoxycarbonylaminophenyl)butyric acid. To a mixture of 4-(4-aminophenyl)butyric acid (3.00 g, 16.7 mmol) in dioxane (25 mL) and water (25 mL) were added triethylamine (3.6 mL, 25.8 mmol) followed by di-*tert*-butyl dicarbonate (5.61 g, 25.7 mmol) in dioxane (25 mL). The reaction mixture was stirred at room temperature for 24 h and quenched slowly by addition of 3 M HCl solution (100 mL) to the reaction mixture. The mixture was extracted with ethyl acetate (3×100 mL). The combined organic layers were washed with brine (2× 60 mL), dried over sodium sulfate and concentrated to furnish the crude product, which was further purified by flash chromatography (silica gel 40 g, ethyl acetate/hexane 1:1). The product (4.36 g, 15.6 mmol, 94%) was isolated as a colorless solid: mp 119.4 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.47 (9H, s), 1.74 (2H, tt, J= 8.2, 7.4 Hz), 2.16 (2H, t, J=7.4 Hz), 2.50 (2H, t, J=8.2 Hz), 7.05 (2H, d, J=8.5 Hz), 7.36 (2H, d, J=8.5 Hz), 9.23 (1H, s); IR (ATR) 1700, 1522 cm^{-1}; MS (CI): *m/z* 223 (100%), 279 ($[M]^+$, 39%); HRMS (CI): calcd for $C_{15}H_{21}NO_4$ ($[M]^+$), 279.1471, found 279.1461. Anal. Calcd for $C_{15}H_{21}NO_4$: C, 64.50; H, 7.58; N, 5.01. Found: C, 64.64; H, 7.77; N, 5.18.

4.2.4. Acylation and Boc-deprotection on the Synphase Lantern. Four hundred and five pieces of the aminomethylated Lantern **8** (D-series, loading: 38 μmol×405, 15.4 mmol) were shaken twice for 10 min in a 1:1 solution (500 mL) of DMF and DCM containing 5% TEA. The solution was removed by decantation and the Lanterns were shaken with a 1:1 solution of DMF and DCM (3×3 min) and DCM (2×10 min). The neutralized Lanterns were reacted with 4-(4-*tert*-butoxycarbonylaminophenyl)butyric acid (8.32 g, 61.6 mmol, 4 equiv), $HOBt\cdot H_2O$ (8.32 g, 61.6 mmol, 4 equiv), and DIC (19.3 mL, 123 mmol, 8 equiv) in a 4:1 solution (220 mL) of DCM and DMF at room temperature for 15 h. The solution was removed by decantation and the Lanterns were washed with DMF (3× 3 min) and DCM (3×3 min). The *N*-protected Lanterns were shaken in DCM (500 mL, 2×3 h) containing 15% TFA. The Lanterns were washed with DMF (3×3 min) and treated with a 1:1 solution (500 mL) of DMF and DCM containing 5% TEA (2×10 min). The solution was removed by decantation and the Lanterns were washed with a 1:1 solution of DMF and DCM (2×10 min) and DCM (2×10 min) to give aniline linker **17**.

Linkers **11**, and **15** were prepared by the same procedure above from **8** and 4-*tert*-butoxycarbonylaminobenzoic acid or 6-(4-*tert*-butoxycarbonylaminophenoxy)hexanoic acid.

4.2.5. Loading of methyl 4-formylbenzoate and cleavage with 4-octyloxyaniline using the resin 8, 11, 15 and 17. Two pieces of the Lantern of the solid supported aniline **17** (A-series, loading 75 μmol×2, 150 μmol) were reacted with methyl 4-formylbenzoate (130.5 mg, 790 μmol, 5.3 equiv) in DMF solution at room temperature for 24 h. The solution was removed by decantation and the Lanterns were washed with DMF (3×0.5 min) and DCM (3× 0.5 min) to give the solid supported ester **18**. The solid supported ester **18** was reacted with 4-octyloxyaniline (132.8 mg, 4 equiv) in DMF (5 mL) at 50 °C for 3 h. The Lanterns were washed with DMF (3×3 min). The combined DMF solution was evaporated and purified by HPLC (hexane/EtOAc 9:1) to give **10** in 94% yield (51.9 mg, 141 μmol) as colorless solid. When the same procedure was applied to the recovered resin, the product **10** was obtained in 89% yield.

The same procedures were also tested to the resin **8**, **11**, and **15**. Their yields were described in the text.

Mp 135.5–136 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (3H, t, J=7.0 Hz), 1.21–1.54 (12H, m), 1.80 (2 H, m), 3.95 (3H, s), 3.98 (2H, d, J=6.6 Hz), 6.94 (2H, d, J=8.8 Hz), 7.27 (2H, d, J=8.8 Hz), 7.96 (2H, d, J=8.4 Hz), 8.13 (2H, d, J=8.4 Hz), 8.54 (1H, s); IR (ATR) 1721, 1621 cm^{-1}; MS (CI): *m/z* 368 ($[M+H]^+$, 100%); HRMS (CI): calcd for $C_{23}H_{30}NO_3$ ($[M+H]^+$), 368.2226, found 368.2235. Anal. Calcd for $C_{23}H_{29}NO_3$: C, 75.17; H, 7.95; N, 3.81. Found: C, 75.14; H, 7.95; N, 3.78.

4.2.6. Loading of 4-formylbenzic acid, condensation with 1-nonanol and cleavage with 4-octyloxyaniline on the resin 15 and 17. Three pieces of the solid supported aniline **17** (A-series, loading 75 μmol×3, 225 μmol) were reacted with 4-carboxybenzaldehyde (179.4 mg, 1.19 mmol, 5.3 equiv) in DMF solution (4 mL) at room temperature for 24 h. The solution was removed by decantation and the Lanterns were washed with DMF (3×0.5 min), and DCM (3×0.5 min) to give the solid supported azomethine **19a**. The azomethine **19a** were reacted with 4-*N*,*N*-dimethylaminopyridine (6.9 mg, 56 μmol, 0.25 equiv), 1-nonanol (157 μL, 900 μmol, 4 equiv) and 1,3-diisopropylcarbodiimide (273 μL, 1.76 mmol, 8 equiv) in DCM (4 mL) at

room temperature for 3 h. The solution was removed by decantation and the Lanterns were washed with DMF (3×0.5 min), and DCM (3×0.5 min) to give the solid supported nonyl ester **22aa**. The solid supported ester **22aa** were reacted with 4-*n*-octyloxyaniline (202 mg, 0.91 mmol, 4 equiv) in DMF (5 mL) at 50 °C for 3 h. The Lanterns were washed with DMF (3×3 min). The combined DMF solution was evaporated and purified by HPLC (hexane/EtOAc 19:1) to give **14aa8** ($n=8$) in 66% yield (71.2 mg, 148 μmol) as pale yellow solid. When the same procedure was applied to the recovered resin, the product **14aa8** was obtained in 40% yield (43.5 mg, 90.7 μmol). The resulting lantern was treated with methyl 4-formylbenzoate (147.7 mg, 900 μmol, 4 equiv) in DMF at 50 °C for 3 h. The Lanterns were washed with DMF (3×3 min). The combined DMF solution was evaporated and purified by HPLC (hexane/EtOAc 4:1) to give **10** in 15% yield (12.4 mg, 33.7 μmol) as pale yellow solid.

The same procedures were also tested to the resin **11**. The product **14aa8** ($n=8$) was obtained in 47% yield (50.8 mg, 106 μmol) as pale yellow solid.

4.3. Parallel synthesis of liquid crystalline library on the solid support 17

4.3.1. Loading of 4-formylbenzic acid (synthesis of 19a). Eighty four pieces of the solid supported aniline **17** (D-series, loading: 38 μmol×84, 3.19 mmol) were reacted with 4-carboxybenzaldehyde (2.54 g, 16.9 mmol, 5.3 equiv) in DMF solution (80 mL) at room temperature for 24 h. The solution was removed by decantation and the Lanterns were washed with DMF (3×0.5 min), and DCM (3×0.5 min).

Compound **19b** was also synthesized by the same procedure as described above.

4.3.2. Condensation with 1-nonanol (synthesis of 22aa). Twenty eight pieces of the solid supported azomethine **19aa** (D-series, loading: 38 μmol×28, 1.06 mmol) were reacted with 4-*N*,*N*-dimethylaminopyridine (32.5 mg, 0.266 mmol, 0.25 equiv), 1-nonanol (0.74 mL, 4.2 mmol, 4 equiv) and 1,3-diisopropylcarbodiimide (1.3 mL, 8.5 mmol, 8 equiv) in DCM at room temperature for 3 h. The solution was removed by decantation and the Lanterns were washed with DMF (3×0.5 min), and DCM (3×0.5 min).

Compounds **22ab**, **22ac**, **22ad**, **22ba** and **22bc** were also synthesized by the same procedure as described above.

4.3.3. Cleavage from the solid support (synthesis of 14aa4). Two pieces of the solid supported ester **22aa** (D-series, loading: 38 μmol×2, 76 μmol) were reacted with 4-*n*-butyloxyaniline (63 mg, 0.38 mmol, 5 equiv) in DMF (5 mL) at 50 °C for 3 h. The Lanterns were washed with DMF (3×3 min). The combined DMF solution was evaporated and purified by HPLC (hexane/EtOAc 19:1) to give **14aa4** ($n=4$) in 55% yield (17.8 mg, 42.0 μmol) as pale yellow solid.

All library members were also synthesized by the same procedure as described above.

All new compounds described gave satisfied spectral and elemental analytic data. One example of spectral data for one homologue of each compound type and only elemental analytic data of new compounds are given.

4.3.3.1. Nonyl 4-[(4-butoxyphenylimino)methyl]benzoate (14aa4, $n=4$). Pale yellow needles; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (3H, t, $J=6.8$ Hz), 0.99 (3H, t, $J=7.1$ Hz), 1.28–1.60 (14H, m), 1.72–1.82 (4H, m), 3.99 (2H, t, $J=6.6$ Hz), 4.34 (2H, t, $J=6.6$ Hz), 6.93 (2H, d, $J=8.8$ Hz), 7.27 (2H, d, $J=8.8$ Hz), 7.95 (2H, d, $J=8.3$ Hz), 8.12 (2H, d, $J=8.3$ Hz), 8.54 (1H, s); IR (ATR) 1710, 1620 cm^{-1}; MS (CI): *m*/*z* 423 ([M]$^+$, 100%); HRMS (CI): calcd for $C_{27}H_{37}NO_3$ ([M]$^+$), 423.2773, found 423.2774. Anal. Calcd for $C_{27}H_{37}NO_3$: C, 76.56; H, 8.80; N, 3.31. Found: C, 76.85; H, 9.09; N, 3.37.

4.3.3.2. Nonyl 4-[(4-pentyloxyphenylimino)methyl]-benzoate (14aa5, $n=5$). Pale yellow needles. Anal. Calcd for $C_{28}H_{39}NO_3$: C, 76.85; H, 8.98; N, 3.20. Found: C, 77.03; H, 9.15; N, 3.28.

4.3.3.3. Nonyl 4-[(4-hexyloxyphenylimino)methyl]-benzoate (14aa6, $n=6$). Pale yellow needles. Anal. Calcd for $C_{29}H_{41}NO_3$: C, 77.12; H, 9.15; N, 3.10. Found: C, 77.30; H, 9.41; N, 3.23.

4.3.3.4. Nonyl 4-[(4-heptyloxyphenylimino)methyl]-benzoate (14aa7, $n=7$). Pale yellow needles. Anal. Calcd for $C_{30}H_{43}NO_3$: C, 77.38; H, 9.31; N, 3.01. Found: C, 77.64; H, 9.50; N, 3.12.

4.3.3.5. Nonyl 4-[(4-octyloxyphenylimino)methyl]benzoate (14aa8, $n=8$). Pale yellow needles. Anal. Calcd for $C_{31}H_{45}NO_3$: C, 77.62; H, 9.46; N, 2.92. Found: C, 77.76; H, 9.74; N, 3.03.

4.3.3.6. Nonyl 4-[(4-nonyloxyphenylimino)methyl]-benzoate (14aa9, $n=9$). Pale yellow needles. Anal. Calcd for $C_{32}H_{47}NO_3$: C, 77.85; H, 9.60; N, 2.84. Found: C, 78.04; H, 9.79; N, 2.99.

4.3.3.7. Nonyl 4-[(4-decyloxyphenylimino)methyl]-benzoate (14aa10, $n=10$). Pale yellow needles. Anal. Calcd for $C_{33}H_{49}NO_3$: C, 78.06; H, 9.73; N, 2.76. Found: C, 78.02; H, 9.50; N, 2.90.

4.3.3.8. 2-(2-Ethoxyethoxy)ethyl 4-[(4-butoxyphenylimino)methyl]benzoate (14ab4, $n=4$). Pale yellow needles; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99 (3H, t, $J=7.3$ Hz), 1.21 (3H, t, $J=7.0$ Hz), 1.51 (2H, qt, $J=7.0$, 6.6 Hz), 1.78 (2H, quint, $J=6.6$ Hz), 3.54 (2H, q, $J=7.3$ Hz), 3.63 (2H, m), 3.71 (2H, m), 3.87 (2H, t, $J=4.8$ Hz), 3.99 (2H, t, $J=6.6$ Hz), 4.52 (2H, t, $J=4.8$ Hz), 6.94 (2H, d, $J=8.8$ Hz), 7.27 (2H, d, $J=8.8$ Hz), 7.95 (2H, d, $J=8.4$ Hz), 8.15 (2H, d, $J=8.4$ Hz), 8.54 (1H, s); IR (ATR) 1705, 1621 cm^{-1}; MS (CI): *m*/*z* 413 ([M]$^+$, 100%); HRMS (CI): calcd for $C_{24}H_{31}NO_5$ ([M]$^+$), 413.2202, found 413.2188. Anal. Calcd for $C_{24}H_{31}NO_5$: C, 69.71; H,7.56; N, 3.39. Found: C, 69.86; H, 7.39; N, 3.44.

4.3.3.9. 2-(2-Ethoxyethoxy)ethyl 4-[(4-pentyloxyphenylimino)methyl]benzoate (14ab5, $n=5$). Pale yellow needles.

Anal. Calcd for $C_{25}H_{33}NO_5$: C, 70.23; H,7.78; N, 3.28. Found: C, 70.27; H, 7.90; N, 3.28.

4.3.3.10. 2-(2-Ethoxyethoxy)ethyl 4-[(4-hexyloxyphenylimino)methyl]benzoate (14ab6, $n=6$). Pale yellow needles. Anal. Calcd for $C_{26}H_{35}NO_5$: C, 70.72; H, 7.99; N, 3.17. Found: C, 70.87; H, 8.10; N, 3.16.

4.3.3.11. 2-(2-Ethoxyethoxy)ethyl 4-[(4-heptyloxyphenylimino)methyl]benzoate (14ab7, $n=7$). pale yellow needles. Anal. Calcd for $C_{27}H_{37}NO_5$: C, 71.18; H, 8.19; N, 3.07. Found: C, 71.43; H, 8.38; N, 2.95.

4.3.3.12. 2-(2-Ethoxyethoxy)ethyl 4-[(4-octyloxyphenylimino)methyl]benzoate (14ab8, $n=8$). Pale yellow needles. Anal. Calcd for $C_{28}H_{39}NO_5$: C, 71.61; H, 8.37; N, 2.98. Found: C, 71.86; H, 8.56; N, 2.97.

4.3.3.13. 2-(2-Ethoxyethoxy)ethyl 4-[(4-nonyloxyphenylimino)methyl]benzoate (14ab9, $n=9$). Pale yellow needles. Anal. Calcd for $C_{29}H_{41}NO_5$: C, 72.02; H, 8.54; N, 2.90. Found: C, 72.29; H, 8.82; N, 3.07.

4.3.3.14. 2-(2-Ethoxyethoxy)ethyl 4-[(4-decyloxyphenylimino)methyl]benzoate (14ab10, $n=10$). Pale yellow needles. Anal. Calcd for $C_{30}H_{43}NO_5$: C, 72.40; H, 8.71; N, 2.81. Found: C, 72.42; H, 8.78; N, 2.85.

4.3.3.15. *S*-Nonyl 4-[(4-butoxyphenylimino)methyl]thiobenzoate (14ac4, $n=4$). Pale yellow needles; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (3H, t, $J=6.6$ Hz), 0.98 (3H, t, $J=7.3$ Hz), 1.20–1.88 (18H, m), 3.09 (2H, t, $J=7.3$ Hz), 3.99 (2H, t, $J=6.2$ Hz), 6.94 (2H, d, $J=9.2$ Hz), 7.27 (2H, d, $J=9.2$ Hz), 7.95 (2H, d, $J=8.1$ Hz), 8.05 (2H, d, $J=8.1$ Hz), 8.53 (1H, s); IR (ATR) 1650, 1620 cm^{-1}; MS (CI): *m/z* 439 ($[M]^+$, 100%); HRMS (CI): calcd for $C_{27}H_{37}NO_2S$ ($[M]^+$), 439.2545, found 439.2569. Anal. Calcd for $C_{27}H_{37}NO_2S$: C, 73.76; H, 8.48; N, 3.19. Found: C, 73.65; H, 8.51; N, 3.24.

4.3.3.16. *S*-Nonyl 4-[(4-pentyloxyphenylimino)methyl]thiobenzoate (14ac5, $n=5$). Pale yellow needles. Anal. Calcd for $C_{28}H_{39}NO_2S$: C, 74.13; H, 8.66; N, 3.09. Found: C, 74.17; H, 8.37; N, 3.25.

4.3.3.17. *S*-Nonyl 4-[(4-hexyloxyphenylimino)methyl]thiobenzoate (14ac6, $n=6$). Pale yellow needles. Anal. Calcd for $C_{29}H_{41}NO_2S$: C, 74.47; H, 8.84; N, 2.99. Found: C, 74.68; H, 9.12; N, 3.08.

4.3.3.18. *S*-Nonyl 4-[(4-heptyloxyphenylimino)methyl]thiobenzoate (14ac7, $n=7$). Pale yellow needles. Anal. Calcd for $C_{30}H_{43}NO_2S$: C, 74.80; H, 9.00; N, 2.91. Found: C, 74.83; H, 9.21; N, 3.00.

4.3.3.19. *S*-Nonyl 4-[(4-octyloxyphenylimino)methyl]thiobenzoate (14ac8, $n=8$). Pale yellow needles. Anal. Calcd for $C_{31}H_{45}NO_2S$: C, 75.10; H, 9.15; N, 2.83. Found: C, 74.87; H, 9.39; N, 2.97

4.3.3.20. *S*-Nonyl 4-[(4-nonyloxyphenylimino)methyl]thiobenzoate (14ac9, $n=9$). Pale yellow needles. Anal. Calcd for $C_{32}H_{47}NO_2S$: C, 75.39; H, 9.29; N, 2.75. Found: C, 75.30; H, 9.53; N, 3.03.

4.3.3.21. *S*-Nonyl 4-[(4-decyloxyphenylimino)methyl]thiobenzoate (14ac10, $n=10$). Pale yellow needles. Anal. Calcd for $C_{33}H_{49}NO_2S$: C, 75.67; H, 9.43; N, 2.67. Found: C, 75.97; H, 9.75; N, 2.84.

4.3.3.22. *N*,*N*-Diisobutyl-4-[(4-butoxyphenylimino)methyl]benzamide (14ad4, $n=4$). Pale yellow needles; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.74 (6H, d, $J=6.6$ Hz), 0.99 (3H, t, $J=7.3$ Hz), 1.01 (6H, d, $J=7.0$ Hz), 1.53 (2H, m), 1.80 (3H, m), 2.14 (1H, m), 3.10 (2H, d, $J=7.3$ Hz), 3.38 (2H, d, $J=7.7$ Hz), 3.99 (2H, t, $J=6.6$ Hz), 6.94 (2H, d, $J=8.8$ Hz), 7.24 (2H, d, $J=8.8$ Hz), 7.45 (2H, d, $J=8.1$ Hz), 7.91 (2H, d, $J=8.1$ Hz), 8.52 (1H, s); IR (ATR) 1622 cm^{-1}; MS (CI): *m/z* 409 ($[M+1]^+$, 100%); HRMS (CI): calcd for $C_{26}H_{37}N_2O_2$ ($[M+H]^+$), 409.2855, found 409.2872. Anal. Calcd for $C_{26}H_{36}N_2O_2$: C, 76.43; H, 8.88; N, 6.86. Found: C, 76.62; H, 9.07; N, 6.89.

4.3.3.23. *N*,*N*-Diisobutyl-4-[(4-pentyloxyphenylimino)methyl]benzamide (14ad5, $n=5$). Pale yellow needles. Anal. Calcd for $C_{27}H_{38}N_2O_2$: C, 76.74; H, 9.06; N, 6.63. Found: C, 76.65; H, 9.37; N, 6.60.

4.3.3.24. *N*,*N*-Diisobutyl-4-[(4-hexyloxyphenylimino)methyl]benzamide (14ad6, $n=6$). Pale yellow needles. Anal. Calcd for $C_{28}H_{40}N_2O_2$: C, 77.02; H, 9.23; N, 6.42. Found: C, 77.19; H, 9.55; N, 6.43.

4.3.3.25. *N*,*N*-Diisobutyl-4-[(4-heptyloxyphenylimino)methyl]benzamide (14ad7, $n=7$). Pale yellow needles. Anal. Calcd for $C_{29}H_{42}N_2O_2$: C, 77.29; H, 9.39; N, 6.22. Found: C, 77.26; H, 9.69; N, 6.22.

4.3.3.26. *N*,*N*-Diisobutyl-4-[(4-octyloxyphenylimino)methyl]benzamide (14ad8, $n=8$). Pale yellow needles. Anal. Calcd for $C_{30}H_{44}N_2O_2$: C, 77.54; H, 9.54; N, 6.03. Found: C, 77.76; H, 9.55; N, 6.06.

4.3.3.27. *N*,*N*-Diisobutyl-4-[(4-nonyloxyphenylimino)methyl]benzamide (14ad9, $n=9$). Pale yellow needles. Anal. Calcd for $C_{31}H_{46}N_2O_2$: C, 77.78; H, 9.69; N, 5.85. Found: C, 77.79; H, 9.97; N, 5.84.

4.3.3.28. *N*,*N*-Diisobutyl-4-[(4-decyloxyphenylimino)methyl]benzamide (14ad10, $n=10$). Pale yellow needles. Anal. Calcd for $C_{32}H_{48}N_2O_2$: C, 78.00; H, 9.82; N, 5.69. Found: C, 78.12; H, 10.04; N, 5.66.

4.3.3.29. Nonyl 4-[(4-butoxyphenylimino)methyl]-3-hydroxybenzoate (14ba4, $n=4$). Yellow needles; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (3H, t, $J=6.8$ Hz), 0.99 (3H, t, $J=6.6$ Hz), 1.25–1.60 (14H, m), 1.70–1.86 (4H, m), 4.00 (2H, t, $J=6.6$ Hz), 4.32 (2H, t, $J=6.6$ Hz), 6.95 (2H, d, $J=9.0$ Hz), 7.30 (2H, d, $J=9.0$ Hz), 7.43 (1H, d, $J=8.1$ Hz), 7.60 (1H, dd, $J=8.1$, 1.1 Hz), 7.67 (1H, d, $J=1.5$ Hz), 8.66 (1H, s); 13.48 (1H, s); 13.50 (1H, s); IR (ATR) 1713, 1616 cm^{-1}; MS (CI): *m/z* 440 ($[M+H]^+$, 100%); HRMS (CI): calcd for $C_{27}H_{38}NO_4$ ($[M+H]^+$), 440.2801, found 440.2799. Anal. Calcd for $C_{27}H_{37}NO_4$: C, 73.77; H, 8.48; N, 3.19. Found: C, 73.79; H, 8.65; N, 3.17.

4.3.3.30. Nonyl 4-[(4-pentyloxyphenylimino)methyl]-3-hydroxybenzoate (14ba5, $n=5$). Yellow needles. Anal. Calcd for $C_{28}H_{39}NO_4$: C, 74.14; H, 8.67; N, 3.09. Found: C, 73.93; H, 8.85; N, 3.09.

4.3.3.31. Nonyl 4-[(4-hexyloxyphenylimino)methyl]-3-hydroxybenzoate (14ba6, $n=6$). Yellow needles. Anal. Calcd for $C_{29}H_{41}NO_4$: C, 74.48; H, 8.84; N, 3.00. Found: C, 74.58; H, 8.51; N, 3.11.

4.3.3.32. Nonyl 4-[(4-heptyloxyphenylimino)methyl]-3-hydroxybenzoate (14ba7, $n=7$). Yellow needles. Anal. Calcd for $C_{30}H_{43}NO_4$: C, 74.81; H, 9.00; N, 2.91. Found: C, 74.60; H, 9.20; N, 2.97.

4.3.3.33. Nonyl 4-[(4-octyloxyphenylimino)methyl]-3-hydroxybenzoate (14ba8, $n=8$). Yellow needles. Anal. Calcd for $C_{31}H_{45}NO_4$: C, 74.96; H, 9.33; N, 2.82. Found: C, 75.14; H, 9.27; N, 2.88.

4.3.3.34. Nonyl 4-[(4-nonyloxyoxyphenylimino)-methyl]-3-hydroxybenzoate (14ba9, $n=9$). Yellow needles. Anal. Calcd for $C_{32}H_{47}NO_4$: C, 75.40; H, 9.29; N, 2.75. Found: C, 75.43; H, 9.52; N, 2.79.

4.3.3.35. Nonyl 4-[(4-decyloxyphenylimino)methyl]-3-hydroxybenzoate (14ba10, $n=10$). Yellow needles. Anal. Calcd for $C_{33}H_{49}NO_4$: C, 75.68; H, 9.43; N, 2.67. Found: C, 75.48; H, 9.03; N, 2.59.

4.3.3.36. *S*-Nonyl 4-[(4-butoxyphenylimino)methyl]-3-hydroxybenzoate (14bc4, $n=4$). Light orange needles; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (3H, t, $J=6.9$ Hz), 0.99 (3H, t, $J=7.1$ Hz), 1.21–1.36 (10H, m), 1.38–1.58 (4H, m), 1.68 (2H, m), 1.79 (2H, m), 3.07 (2H, t, $J=7.1$ Hz), 4.00 (2H, t, $J=6.3$ Hz), 6.95 (2H, d, $J=9.1$ Hz), 7.30 (2H, d, $J=9.1$ Hz), 7.43 (1H, d, $J=8.0$ Hz), 7.50 (1H, dd, $J=8.0$, 1.6 Hz), 7.59 (1H, d, $J=1.6$ Hz), 8.65 (1H, s), 13.55 (1H, s); IR (ATR) 1651, 1626 cm^{-1}; MS (CI): *m/z* 456 ($[M+H]^+$, 100%); HRMS (CI): calcd for $C_{27}H_{38}NO_3S$ ($[M+H]^+$), 456.2572, found 456.2589. Anal. Calcd for $C_{27}H_{37}NO_3S$: C, 71.17; H, 8.18; N, 3.07. Found: C, 71.21; H, 8.29; N, 3.45.

4.3.3.37. *S*-Nonyl 4-[(4-pentyloxyphenylimino)-methyl]-3-hydroxybenzoate (14bc5, $n=5$). Light orange needles. Anal. Calcd for $C_{28}H_{39}NO_3S$: C, 71.60; H, 8.37; N, 2.98. Found: C, 71.80; H, 8.52; N, 3.07.

4.3.3.38. Nonyl 4-[(4-hexyloxyphenylimino)methyl]-3-hydroxybenzoate (14bc6, $n=6$). Light orange needles. Anal. Calcd for $C_{29}H_{41}NO_3S$: C, 72.01; H, 8.54; N, 2.90. Found: C, 72.27; H, 8.80; N, 2.96.

4.3.3.39. *S*-Nonyl 4-[(4-heptyloxyphenylimino)-methyl]-3-hydroxybenzoate (14bc7, $n=7$). Light orange needles. Anal. Calcd for $C_{30}H_{43}NO_3S$: C, 72.39; H, 8.71; N, 2.81. Found: C, 72.38; H, 8.96; N, 2.92.

4.3.3.40. *S*-Nonyl 4-[(4-octyloxyphenylimino)methyl]-3-hydroxybenzoate (14bc8, $n=8$). Light orange needles. Anal. Calcd for $C_{31}H_{45}NO_3S$: C, 72.76; H, 8.86; N, 2.74. Found: C, 73.02; H, 9.13; N, 2.81.

4.3.3.41. *S*-Nonyl 4-[(4-nonyloxyphenylimino)-methyl]-3-hydroxybenzoate (14bc9, $n=9$). Light orange needles. Anal. Calcd for $C_{32}H_{47}NO_3S$: C, 73.10; H, 9.01; N, 2.66. Found: C, 73.08; H, 9.27; N, 2.73.

4.3.3.42. *S*-Nonyl 4-[(4-decyloxyphenylimino)methyl]-3-hydroxybenzoate (14bc10, $n=10$). Light orange needles. Anal. Calcd for $C_{33}H_{49}NO_3S$: C, 73.42; H, 9.15; N, 2.59. Found: C, 73.70; H, 9.44; N, 2.68.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2005.08.086

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